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METHOD FOR MANUFACTURING CLAY-DOPED RUBBER COMPOSITE MATERIAL

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[There are no amendments to this patent.]

Abstract

Objective

The objective of this invention is to provide a method for manufacturing clay-doped rubber composite material characterized by the fact that a clay mineral can be dispersed homogeneously in rubber.

Constitution

A type of clay-doped rubber composite material characterized by the fact that it is manufactured as follows: the inorganic ions of a clay mineral are ion-exchanged with organic onium ions so that the clay mineral is converted to an organic form; then, the organic form of the clay mineral and a process oil for rubber and/or plasticizer are mixed, followed by mixing with a rubber material so that said clay mineral is dispersed homogeneously in the rubber material. It is preferred that the organic onium ions have a carbon number of 6 or larger, the process oil for rubber be a paraffin-based oil, naphthene-based oil or aroma [transliteration]-based oil, and the plasticizer be an ester-based compound, phosphoric ester-based compound or sulfonamide-based compound.

//see orig. p. 1//

Key: 1 Process oil for rubber and/or plasticizer
 7 Clay mineral

Claims

1. A method for manufacturing clay-doped rubber composite material characterized by the fact that said composite material is manufactured as follows: the inorganic ions of a clay mineral are ion-exchanged with organic onium ions so that the clay mineral is converted to an organic form; then, the organic form of the clay mineral and a process oil for rubber and/or plasticizer are mixed, followed by mixing with a rubber material so that said clay mineral is dispersed homogeneously in the rubber material.

2. The method for manufacturing clay-doped rubber composite material described in Claim 1, characterized by the fact that said process oil for rubber refers to one or more selected from the group of paraffin-based oils, naphthene-based oils or aroma based oils.

3. The method for manufacturing clay-doped rubber composite material described in Claim 1 or 2, characterized by the fact that said plasticizer refers to one or more selected from the group of ester-based compounds, phosphoric ester-based compounds and sulfonamide-based compounds.

4. The method for manufacturing clay-doped rubber composite material described in any of Claims 1-3, characterized by the fact that said rubber material refers to one or more selected from the group of natural rubber, isoprene rubber, chloroprene rubber, styrene rubber, nitrile rubber, ethylene-propylene rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, epichlorohydrin rubber, acrylic rubber, urethane rubber, fluorine rubber, and silicone rubber.

Detailed explanation of the invention

[0001]

Field of the technology

This invention pertains to a method for manufacturing clay-doped rubber composite material with a clay mineral dispersed on the molecular level in the rubber.

[0002]

Prior art

In the prior art, in order to improve the mechanical characteristics of rubber material, studies have been made on adding and mixing clay minerals. For example, Japanese Kokai Patent Application No. Hei 1[1989]-198645 disclosed a method in which a clay mineral is converted to organic form by means of an oligomer prepared by introducing onium ions onto the terminals or side chains, and the organic form of a clay mineral is mixed in the rubber material. Japanese Kokai Patent Application No. Sho 60[1985]-4541 also disclosed a method in which mica is first processed with ammonium chloride or chlorinated choline and it is then blended with a rubber material, so that a rubber material with mica dispersed homogeneously in it is obtained.

[0003]

Problems to be solved by the invention

However, the aforementioned conventional clay-doped rubber composite material has some problems. First of all, for said former technology disclosed in Japanese Kokai Patent Application No. Hei 1[1989]-198645, preparation of the oligomer with onium ions introduced in

it is not an easy job. Because the oligomer is directly introduced between the layers of the clay mineral, interlayer swelling of the clay mineral may also be insufficient.

[0004]

On the other hand, for the technology disclosed in Japanese Kokai Patent Application No. Sho 60[1985]-4541, although a process oil is added during blending, the affinity between said processed mica and the process oil is nevertheless poor, and, as the amount of the process oil added is increased, it becomes harder to disperse the mica. This is undesired.

[0005]

The objective of this invention is to solve the aforementioned problems of the conventional methods by providing a method for manufacturing a type of clay-doped rubber composite material characterized by the fact that the clay mineral can be dispersed homogeneously in the rubber.

[0006]

Means to solve the problems

The invention in Claim 1 provides a method for manufacturing clay-doped rubber composite material characterized by the fact that said composite material is manufactured as follows: the inorganic ions of a clay mineral are ion-exchanged with organic onium ions so that the clay mineral is converted to an organic form; then, the organic form of the clay mineral and a process oil for rubber and/or plasticizer are mixed, followed by mixing with a rubber material so that said clay mineral is dispersed homogeneously in the rubber material.

[0007]

In the following, the function and effect of this invention will be explained. Although the clay mineral usually displays an excellent swelling property in water, it is difficult to swell in an organic solvent. According to this invention, inorganic ions, such as Na ions, Li ions, etc., present between layers of the clay mineral, are ion-exchanged with the onium ions, the clay mineral is converted to an organic form, so that the clay mineral becomes hydrophobic. As a result, interlayer swelling of the clay mineral can be realized in a hydrophobic organic solvent.

[0008]

Then, as explained above, a process oil for rubber and/or a plasticizer is added between the layers of the organic form of the clay mineral, followed by blending with a rubber material.

In this way, even for the rubber material, in which dispersion of the clay mineral used to be difficult, the clay mineral still can be dispersed homogeneously with a large interlayer distance.

[0009]

The reason is believed to be as follows. As shown in Figure 1, clay mineral (7) is converted to an organic form by organic onium ions (6), so that large spaces are formed between layers of clay mineral (7). Consequently, it is possible to accommodate the process oil for rubber and/or plasticizer (1) between layers.

[0010]

The affinity between the process oil for rubber and/or plasticizer and the rubber material is also good. Consequently, the rubber material fits well with the process oil for rubber and/or plasticizer, and it can penetrate between the layers of the clay mineral. Consequently, the interlayer swelling of the clay mineral becomes significant. As a result, the clay mineral can be dispersed homogeneously in the rubber material.

[0011]

As explained above, because the clay mineral can be dispersed homogeneously in the rubber material, its ability to block gas, water, etc., is improved. Also, movement of the rubber molecules near the silicate layer is restrained. Consequently, the mechanical characteristics of the clay-doped rubber composite material are improved.

[0012]

The clay-doped rubber composite material manufactured in this invention can be used in various applications of conventional rubber materials. In particular, the effect of this invention can be best displayed when a high barrier property against water, gas, etc., or better mechanical properties of the rubber material are required.

[0013]

In the following, this invention will be explained in detail. As far as the aforementioned clay mineral is concerned, a type with a large contact area with the process oil for rubber and/or plasticizer is preferred, because in this case, the interlayer of the clay mineral can undergo even greater swelling. More specifically, a clay mineral with a cation exchange capacity in the range of 50-200 mEq/100 g is preferred. If this exchange capacity is lower than 50 mEq/100 g, exchange with the onium ions cannot be sufficiently carried out, and interlayer swelling of the clay mineral may be difficult. On the other hand, if the exchange capacity is higher than

200 mEq/100 g, the interlayer bonding of the clay mineral becomes stronger, and interlayer swelling may be difficult.

[0014]

Examples of said clay minerals that may be used include montmorillonite, saponite, hectorite, beidellite, stevensite, nontronite, and other smectite-based clay minerals, vermiculite, halloysite, swelling fluorine mica, etc. Both natural and synthetic types may be used.

[0015]

Said clay mineral is converted to an organic form by means of ion-exchange with organic onium ions. It is preferred that said organic onium ions have a carbon number of 6 or larger, or more preferably in the range of 6-40, or most preferably in the range of 6-30. In this way, it is possible to realize good interlayer swelling of the clay mineral together with the process oil for rubber and/or plasticizer.

[0016]

Examples of said onium ions include hexylammonium ions, octylammonium ions, 2-ethylhexylammonium ions, dodecylammonium ions, octadecylammonium ions, dioctyldimethylammonium ions, trioctylammonium ions, distearyl dimethylammonium ions, etc.

[0017]

In addition, the following scheme may also be adopted: the clay mineral is converted to an organic form by means of organic onium ions; then, the clay mineral is mixed with an oligomer containing polar groups, followed by heating or other treatment; then, swelling is performed by means of the process oil for rubber and/or plasticizer. Examples of the aforementioned oligomer containing said polar groups include hydrogenated polybutadiene oligomer (Polytel H [transliteration] manufactured by Mitsubishi Chemical Co., Ltd., etc.), polyisoprene oligomer (LIR 506 manufactured by Kuraray, etc.), etc.

[0018]

Then, the organic form of the clay mineral is mixed with the process oil for rubber and/or plasticizer. In this case, said process oil for rubber refers to the petroleum-based oils used for improving the processability of the rubber.

[0019]

There is no special limitation on said process oil for rubber. For example, as in Claim 2 of this invention, said process oil for rubber is preferably one or more selected from the groups of paraffin-based oils, naphthene-based oils or aroma based oil. In this way, interlayers of the clay mineral can undergo better swelling.

[0020]

Examples of said paraffin-based oils include the following products of Idemitsu Kosan Co., Ltd.: PX-90, PW-90, PS-90, and PW-380. Examples of said naphthene-based oils include Flex 1400N manufactured by Fuji Kosan Co., Ltd., Sunsene [transliteration] 459 manufactured by Nippon Sun Petroleum Co., Ltd., NS-100 manufactured by Idemitsu Kosan Co., Ltd., NM-280 manufactured by Idemitsu Kosan Co., Ltd., etc. Examples of said aroma based oils include AC-460 and AH-58 manufactured by Idemitsu Kosan Co., Ltd., etc. Among these process oils for rubber, in particular, naphthene-based oils are preferred in consideration of the interlayer swelling property of the clay mineral and affinity for the rubber material.

[0021]

There is no special limitation on the type of said plasticizer. For example, according to the invention in Claim 3, said plasticizer is preferably one or more selected from the group of ester-based compounds, phosphoric ester-based compounds and sulfonamide-based compounds. In this way, it is possible to have even greater interlayer swelling of the clay mineral.

[0022]

Examples of said ester-based compounds that may be used include dibutyl phthalate, butylbenzyl phthalate, ethylphthalyl ethyl glycolate, dibutyl sebacate, methylacetyl ricinoleate, di-2-ethylhexyl adipate, di-2-ethylhexyl azelate, etc. Examples of said phosphoric ester-based compounds include tributyl phosphate, etc. Examples of said sulfonamide-based compounds include N-butylbenzene sulfonamide, etc.

[0023]

For example, as described in Claim 4 of this invention, said rubber material refers to one or more selected from the group of natural rubber, isoprene rubber, chloroprene rubber, styrene rubber, nitrile rubber, ethylene-propylene rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, epichlorohydrin rubber, acrylic rubber, urethane rubber, fluorine rubber, and silicone rubber.

[0024]

The mixing ratio of said organic form of clay mineral to the process oil for rubber and/or plasticizer is preferably in the range of 10:1~100. In this way, it is possible to realize great interlayer swelling of the clay mineral. If the aforementioned mixing ratio is 10 of the clay mineral:less 1, a great interlayer swelling of the clay mineral may be difficult to perform. On the other hand, if the ratio is 10:over 100, the properties of the rubber may be degraded.

[0025]

When the organic onium ions are ion-exchanged, for example, the clay mineral is well dispersed in water. Then, the organic onium ions are added to form an organic form of the clay mineral. When the organic form of the clay mineral and the process oil for rubber and/or plasticizer are mixed, the mixing temperature may be at room temperature. However, it is preferred that the mixing temperature be raised to 150°C. In this way, the organic form of the clay mineral can undergo swelling at a high efficiency.

[0026]

Then, the swelled clay mineral is blended with the rubber material. In this case, it is preferred that a mixing roll, banbury mixer, biaxial extruder, or other blending device be used. In this way, it is possible to perform blending at a high efficiency. Among these devices, the mixing roll is preferred. The blending temperature is preferably in the range from room temperature to 150°C. In this way, it is possible to perform sufficient blending.

[0027]

Also, during blending, it is possible to add an appropriate amount of carbon black, curing agent, curing promoter, etc., which are added in the conventional rubber material. The blend of the swollen clay mineral and the rubber material can be processed by press formation or other conventional rubber curing method to manufacture a molding.

[0028]

Embodiments

Embodiment Example 1

This embodiment example of the invention pertains to a method for manufacturing a clay-doped rubber composite material. The method for manufacturing the clay-doped rubber composite material can be explained briefly as follows. First of all, the inorganic ions of a clay mineral are ion-exchanged with organic onium ions so that the clay mineral is converted to an organic form; then, the clay mineral and a process oil for rubber are mixed, followed by mixing

with a rubber material so that said clay mineral is dispersed homogeneously in the rubber material.

[0029]

As the clay mineral, sodium montmorillonite (product of Yamagata Prefecture, with ion-exchange capacity of 120 mEq/100 g) was used. As the organic onium ions, distearyldimethylammonium ions with carbon number 38 were used. As the process oil for rubber, Flex 1400N (product of Fuji Kosan Co., Ltd.) was used. As the rubber material, natural rubber was used.

[0030]

In the following, the method for manufacturing said clay-doped rubber composite material will be explained in detail. First of all, 20.0 g of montmorillonite were dispersed in 2000 mL of water at 80°C. Then, 21.0 g of stearyl dimethylammonium chloride were dissolved in 1500 mL of water at 80°C. Said dispersion and said solution were mixed with each other all at once. The precipitate was washed twice with water at 80°C, forming montmorillonite converted to an organic form by the distearyldimethylammonium ions. This will be referred to as DSDM-montmorillonite hereinafter.

[0031]

The inorganic content in the DSDM-montmorillonite was derived using the ignition method and was found to be 54.2 wt%. By means of X-ray diffraction, the interlayer distance of DSDM-montmorillonite was measured, and the swelling performance was observed. It was found that the interlayer distance of DSDM-montmorillonite is 36.5 Å.

[0032]

Then, 1.0 g of said DSDM-montmorillonite and 1.0 g of Flex 1400N were mixed at 80°C for 12 h to form a clay composite material. Then, X-ray diffraction was used to measure the interlayer distance of montmorillonite in the clay composite material, and it was found to be 46.5 Å. This fact indicates that by adding a process oil for rubber, the interlayer distance of montmorillonite becomes greater than when it is not added, so that swelling takes place. Also, this indicates that the process oil for rubber penetrates between layers of montmorillonite.

[0033]

Then, 20 parts by weight of said clay composite material (containing 10 parts by weight of the clay mineral) were mixed with 100 parts by weight of the natural rubber, 3 parts by weight

of zinc bloom, 2.25 parts by weight of sulfur and 2 parts by weight of curing promoter. The mixture was blended homogeneously to form a blend. This blending operation was performed by rolls according to ASTM D 3184.

[0034]

The blend was cured at 160°C for 10 min, and it was formed into a sheet with a thickness of 2 mm. From this sheet, dumbbell No. 3 specimens were cut out for tensile testing. As a result, it was found that the tensile strength was 27.5 MPa. Also, the sheet was examined by transmission electron microscopy, and it was found that a silicate layer (montmorillonite) with thickness of 1 nm was dispersed homogeneously in the rubber. Also, a 0.5-mm-thick sheet was formed in the same way as above for evaluation of water permeability. The water permeability was found to be $3.9 \times 10^{-5} \text{ g}\cdot\text{mm}/\text{mm}^2\cdot\text{day}$.

[0035]

Comparative Example 1

In this example, no clay composite material was added, and a sheet was manufactured from a rubber material. That is, 100 parts by weight of natural rubber, 3 parts by weight of zinc bloom, 2.25 parts by weight of sulfur, and 2 parts by weight of curing promoter were blended homogeneously, and the blend was formed into a sheet in the same way as in said Embodiment Example 1. It was found that the tensile strength of the sheet was 22.7 MPa, and the water permeability was $6.5 \times 10^{-5} \text{ g}\cdot\text{mm}/\text{mm}^2\cdot\text{day}$.

[0036]

Embodiment Example 2

In this example, a plasticizer was used to manufacture a clay-doped rubber composite material. The clay mineral was converted to an organic form by octadecylammonium ions. As the plasticizer, methylacetyl ricinoleate was used. As the rubber material, EPDM (ethylene-propylene-diene terpolymer, same in the following) (commercial name EP22, product of Nippon Synthetic Rubber Co., Ltd.) was used.

[0037]

In the following, the method for manufacturing said clay-doped rubber composite material will be explained in detail. First of all, 20.0 g of montmorillonite were dispersed in 2000 mL of water at 80°C. Then, 8.8 g of octadecylammonium chloride were dissolved in 1500 mL of water at 80°C. Said dispersion and said solution were mixed with each other all at once. The precipitate was washed twice with water at 80°C, forming montmorillonite converted

to an organic form by the octadecylammonium ions. This will be referred to as C18-montmorillonite hereinafter.

[0038]

The inorganic content in the C18-montmorillonite was derived using the ignition method and was found to be 69.5 wt%. By means of X-ray diffraction method, the interlayer distance of C18-montmorillonite was measured. It was found that the interlayer distance of C18-montmorillonite is 22.5 Å.

[0039]

Then, 1.0 g of said montmorillonite and 1.0 g of methylacetyl ricinoleate were mixed at 80°C for 4 h to form a clay composite material. Then, the X-ray diffraction method was used to measure the interlayer distance of montmorillonite in the clay composite material, and it was found to be 50.7 Å. This fact indicates that by adding a plasticizer, the interlayer distance of montmorillonite becomes greater than when it is not added, so that swelling takes place. This also indicates that the plasticizer penetrates between the layers of montmorillonite.

[0040]

Then, 20 parts by weight of said clay composite material (containing 5 parts by weight of the clay mineral) were mixed with 100 parts by weight of EPDM, 20 parts by weight of carbon (Asahi Carbon #70), 3 parts by weight of zinc bloom, 1.5 parts by weight of sulfur and 1 part by weight of curing promoter. The mixture was blended homogeneously to form a blend. This blending operation was performed by rolls according to ASTM D 3568.

[0041]

The blend was cured at 160°C for 30 min, and it was formed into a sheet with a thickness of 2 mm. From this sheet, dumbbell No. 3 specimens were cut out for tensile testing. As a result, it was found that the tensile strength was 20 MPa. The sheet was examined by transmission electron microscopy, and it was found that a silicate layer (montmorillonite) with thickness of 1 nm was dispersed homogeneously in the rubber. A 0.5-mm-thick sheet was also formed in the same way as above for evaluation of water permeability. The water permeability was found to be $1.0 \times 10^{-6} \text{ g}\cdot\text{mm}/\text{mm}^2\cdot\text{hr}$ [sic].

[0042]

Comparative Example 2

In this example, the clay composite material was not added, and a sheet was manufactured from a rubber material. That is, 100 parts by weight of EPDM, 20 parts by weight of carbon, 3 parts by weight of zinc bloom, 1.5 parts by weight of sulfur, and 1 part by weight of a curing promoter were blended homogeneously, and the blend was formed into a sheet in the same way as in Embodiment Example 2. It was found that the sheet had a tensile strength of 12.0 MPa and a water permeability of $1.2 \times 10^{-6} \text{ g} \cdot \text{mm}/\text{mm}^2 \cdot \text{day}$.

[0043]

Effect of the invention

According to this invention, it is possible to provide a method for manufacturing a type of clay-doped rubber composite material characterized by the fact that a clay mineral can be dispersed homogeneously in a rubber.

Brief description of the figures

Figure 1 is a diagram illustrating the clay-doped rubber composite material in this invention.

Explanation of reference numbers

- 1 Process oil for rubber and/or plasticizer
- 6 Organic onium ions
- 7 Clay mineral

Figure 1

Key: 1 Process oil for rubber and/or plasticizer
7 Clay mineral